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## **XRF Analysis of Maya Ceramics at Tipu and San Pedro, Belize**

Molly R. Carney

Whenever the Maya are mentioned, large sweeping pyramids and vast jungle cities often come to mind. Most people associate the Maya with the Classic period, which ranged from A.D. 300–900 and is often considered the height of Maya civilization. The Maya “collapse” took place around A.D. 800–900 and constituted a decline and abandonment of Maya centers in the southern lowlands. However, the Postclassic period marked a time of florescence in the northern lowlands. Tipu, located near the Belize-Guatemala border in western Belize, and San Pedro, located on Ambergris Caye off the coast of Belize, are both Maya sites with Postclassic period Maya occupation. The Postclassic period ranged from A.D. 900–1521 and marks the time after the Classic period collapse up until Spanish contact. Long thought of as a period of cultural decline, the Postclassic Maya period is now believed to be one of exchange, commercialism, and extensive trade (Aimers personal communication 2011). There is evidence of this extensive trade along the Caribbean coasts and rivers, and inland at sites such as Mayapan and Chichen Itza.

According to Rice (2012) a study of a collection of archaeological pottery generally proceeds in three steps: classification, analysis, and finally interpretation and explanation. For the purpose of this study, we are attempting to chemically classify examples of two closely related types—Payil Red and Palmul Incised from the Red Payil Group of Tulum Red Ware excavated at the sites of Tipu and San Pedro. While these two types appear stylistically very similar, do they have the same chemical signatures? By analyzing the chemical makeup of these pottery samples we hope to see if the stylistic classification corresponds with the chemistry. The ultimate purpose of this study is to assess and compare Tipu and San Pedro pottery sherd samples through stylistic classification and chemical analysis to further understand trade and exchange routes in the Maya Postclassic.

## Classification of Pottery

Why is it important and necessary to categorize pottery sherds? Classifications help to organize and structure data. Pottery can provide clues to the culture, history, trade and exchange routes, and time period of the people who used it. Pottery, when classified consistently, can provide a reliable method of achieving relative or correlated dates for time periods across Maya settlements. This can help us to better understand chronology and be used a basis for inferences about Maya life (Smith, Wiley, & Gifford 1960:330). It is important to note that there is no “correct” way to classify pottery—we categorize ceramics in order to establish potential answers to analytic questions. In this study, we used type-variety to categorize the ceramic sherds. Type-variety has been the dominant classification system for the analysis of Maya pottery for many years.

Essentially, the type-variety system is a hierarchical system of classification used to stylistically characterize pottery (Rice 1982:282). It was first used in the American Southwest and then adapted to Maya pottery. The type-variety system has four major levels: ware, group, type, and variety. Ware is a broad and inclusive category defined by the pottery’s finish or paste/fabric. Groups are used to aggregate or “lump” types that are very closely related and have similar attributes, such as the Payil Group under investigation here. The third category, type, is where classification gets more specific and is what our study is concerned with. Types are defined by distinct clusters of attributes that are indicative of a particular class of pottery produced during a specific time interval in a specific region (Smith, Willey, & Gifford 1960:333). Type names are usually binomial with a place name as the first part of the type and a descriptive term as the second part of the type name. For example, the type name Payil Red follows these rules of a location and a descriptive word. Finally, varieties are the smallest meaningful unit in classification. They are subsets of types (or subtypes) based on one or more minor attributes. Varieties may be very local or limited in time. Previously, all classification work on pottery sherds at Geneseo was done through type-variety classification.

However, this study uses elemental and mineralogical analytical techniques in an attempt to examine the assigned classifications. Mineralogical analysis involves looking at the larger crystalline components of the ceramic paste (Rice 1987:372). X-ray diffraction is one method used to determine the mineralogical composition of samples. X-rays are shot at a powdered

sample and the angle of reflection is measured and used to determine the minerals within. While X-ray diffraction is a proposed part of the study, the pottery samples have not yet been run.

This study instead focused on assessing the chemical composition of the ceramic sherds. Chemical analysis identifies the chemical elements or compounds constituting the ceramic (Rice 1982:372). X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) are the two main methods of determining elemental composition. However, as INAA is extremely costly and needs a nuclear reactor, which is not available at SUNY Geneseo, this study used XRF to analyze the composition of the sherds. X-ray fluorescence is a technique used to identify the chemical composition of a sample. First, a beam of x-rays is aimed at the sample. The electromagnetic radiation of the x-rays can cause the elements in the sample to become ionized. The energy from the radiation causes an electron to be emitted, and energy is released. This energy, also emitted as radiation, is called fluorescence. The amount of energy emitted is different for each element, thus allowing us to analyze the levels of fluorescence to identify the elemental composition of the sample. This method works well for elements Na (atomic number 11) to antimony (atomic number 51) (Shackley 2010). By studying the levels of energy emitted, we can determine which elements are present in a sample.

Nineteen samples from Tipu and 20 samples from San Pedro were included in this study. The majority of the samples, as previously mentioned, were of the closely related Red Payil or Palmul Incised types. Payil Red is a plain red type of Maya pottery and Palmul Incised is simply its incised version. These two types are believed to have been produced along the coast of the Mexican state of Quintana Roo at the sites of Ichpaatun, Tancah, and Tulum (Sanders 1960). These similar types were chosen in order to compare stylistic classifications with the elemental signatures of the ceramics. These types are so consistent that there are only so many stylistic, macroscopic details that can be assessed, and this study is designed to assess the chemical variability within these two related types. As these types are so closely related, there are no defined varieties underneath the types. It will be interesting to see if the chemical analysis will allow us to determine separate technological varieties under the stylistically similar types. Three extra samples from Tipu that fell outside the Red Payil Group were also analyzed. These samples, T-17A and T-17B, of the Augustine Red type, and T-18, which is Pozo Unslipped, were included to see how much the chemical results varied for sherds that are macroscopically quite different from Red Payil Group sherds.

## **Why Study Pottery Sherds?**

The overarching question remains—what is the purpose of this study? Why is it important to understand similarities and differences in ancient Maya pottery? What is the grand significance?

Scientifically speaking, the purpose of the study is to determine whether the assigned ceramic classifications correlate with the chemical composition of the sample sherds. This study is an effort to see if the stylistic and chemical classifications align. Because the pottery sherds under investigation here are common and widely distributed, it will be interesting to see if chemical subtypes can be created from the macroscopically visible main types.

Yet there is much more to learn from the pottery than just the chemical composition and how that changes classification. Through studying the results of the elemental analysis we also hope to discover a “recipe” for the ceramics, which might shed light on the original potters’ decisions regarding their work. This allows archaeologists to gain insight into the consumption and production of Maya ceramics. Through this study, we hope to further understand Maya consumer choices. How were certain pots made? How many different recipes were used? How far were they traded? Through results from this study and further analysis we hope to answer questions like these.

A final application of this study is to assess exchange and trade routes throughout the modern-day country of Belize as seen in the Maya Postclassic period. Ethnohistorical research indicates that Tipu was closely linked with various independent sites of the Peten Lakes region of Guatemala and other burgeoning Postclassic sites (Aimers personal communication 2011). These connections indicate extensive trade in a time period once called a “decline” or “collapse.” As archaeological material from this time is relatively rare, the Tipu and San Pedro collections offer great potential for research and analysis. So, this research is one part of a much larger investigation that will involve multiple types from many sites, and eventually comparison with the distribution patterns of obsidian.

## **Sample Preparation**

Geneseo’s XRF spectrometer requires samples to be ground into powder and fused into either a glass bead, for identifying major elements, or a wax pellet, which is used to identify trace elements. The first step for each sample involved removing all materials from the surface of the sherd. This was done in order to analyze the elemental composition of the actual pottery body or

paste, and not any other foreign substances on the surface or the applied slip. For each sample, I used a silicon carbide burr to “sand” and remove the slip or any other materials from the surface. Slip is a fluid suspension of fine clay and water used to coat a ceramic vessel before firing and is often considered a stylistic classification attribute (Rice 1987:482). After this was completed, I broke off a piece of the sherd of about 12 grams using pliers. I cleaned the broken pottery to remove any soil and debris, and then broke up the sample into smaller pieces.

The next step involved grinding the sample into a fine, homogenized powder. The broken sample pieces were placed into a metal shaker with two metal balls inside to crush the pottery. The sample was placed into a ball mill and run for about four minutes. After that time I checked the sample to see if all pieces had been ground into a fine powder. If there were any solid pieces left, I ran the sample for another four minutes to ensure that the sample was fully powdered. The powdered sample was then added to a labeled plastic vial, and the ball mill shaker cleaned with sand before a new sample was run.

After powdering, I created the glass bead and wax pellet samples that would be run in the XRF spectrometer. Glass beads are used in XRF to identify the major elements composing the pottery, while wax pellets are used in identifying the trace elements. For the glass beads, six grams of flux was measured and added to a vial, and then .5 grams of powdered sample was measured and blended in with the flux. While most of the Tipu samples did successfully create glass beads, the fluxer machine was nonfunctional during my time in the lab and I personally never had the chance to create any glass beads.

However, this was not a total failure, as it is the trace elemental analysis that tells us more about the pottery. Rice notes, “Trace elemental analyses are based on the principle that most naturally occurring substances contain minute amounts of certain rare or trace elements. The combination and concentration of these elements are unique to their source and will vary considerably from the trace components in similar materials having a different source” (1978:513). To create the wax pellets used in trace elemental analysis, I measured out six grams of powdered sample and blended it with 1.5 grams of binder. Then using the die press machine in the lab, I put the sample under 20 metric tons of pressure for five minutes to create the wax pellet.

The finished samples were then run in the XRF spectrometer. Samples were carefully loaded with the homogenous side facing the laser beam and analyzed using SuperQ Manager

software, a process that took about two hours to complete. The results were then loaded into an Excel spreadsheet for further analysis and interpretation.

### **Potential Problems With XRF Analysis**

Despite the best efforts and intentions, experiments can go wrong. There are several important issues to consider when analyzing elements in ceramics. The first, and most prevalent, issue with obtaining accurate results is inexperience. Shackley (2010) writes that with XRF technology there is the "...issue of poor scientific training by American archaeologists." Archaeologists are not chemists, and many archaeologists who undertake XRF studies do not know how XRF works or how to properly prepare samples. Shackley continues, "...archaeologists are interested in science, but are not necessarily trained in a scientific discipline." This cautionary statement addresses the fact that archaeologists have been guilty of rushing into XRF studies without proper knowledge and training. This whole study has been an exercise in learning, as the techniques were new to both my mentor and me.

This especially comes into play when Portable X-Ray Fluorescence (PXRF) is taken into consideration. PXRF machines have, within the past 10 years, frequently come into the hands of inexperienced archaeologists. Compared with INAA and XRF, PXRF is nondestructive and can be used on ceramics and archaeological material finds without causing any damage. These machines allow archaeologists to simply point a laser at an object and obtain quick results without the hassle of "traditional" sample preparation. However, the lack of experience and knowledge can lead to skewed results.

Although PXRF is theoretically non-destructive, to correctly analyze ceramics the surface must be clear of paint, glaze, dirt, etc. While an acceptable surface may be found on the pottery, better and more accurate results will be obtained when the surface has been abraded or the sample has been prepared as a pressed pellet or fused disk (Speakman et al. 2011:3484).

Another issue that archaeologists must contend with is the accuracy of PXRF machines. In a study by Speakman et al., ceramic pottery samples from the American Southwest was analyzed by a PXRF instrument and through INAA. All samples were carefully prepared (INAA samples were cleaned and powdered and PXRF samples abraded on the surface and then cleaned) and chosen from a collection of well-studied pottery. The researchers found that some elements correlate well between the two analytical methods, while others had lower correlations. Rubidium (Rb), Strontium (Sr), and Iron (Fe) all correlated well. However, Thorium (Th) and

Aluminum (Al) had low correlation ratios. When the major elemental data was separated into groups, the PXRF data did not fall into distinct, chemically separate groups. Groups based upon chemical makeup were much clearer with INAA. The study concluded, “Although there is not a direct 1:1 correlation between the two datasets, data from the portable XRF study are somewhat in agreement with the corresponding INAA data... Despite the generally acceptable results from portable XRF, it is clear that INAA has significantly greater analytical precision. In addition, the ability of INAA to measure trace and rare earth elements has proved critical to being able to effectively identify compositional groups that are useful for provenance studies” (Speakman et al.).

Another problem that crops up with ceramic chemical analysis is the idea that archaeologists make certain assumptions when dealing with ceramics. Rice challenges the basic assumption in ceramic studies is that “...at no time during pottery manufacture or use...is the trace element configuration characteristic of a raw clay deposit significantly altered” (1978:514). In order to assign pottery to a specific manufacture area, archaeologists assume that the geochemistry and availability of clay deposits have not changed in the intervening time, that the potters have not significantly altered the clay, that firing time and temperature will not affect trace element composition, and that post-depositional alteration does not introduce or leach out elements (i.e., the ceramic chemical makeup does not change once it has been discarded due to environment) (Rice 1978:515–517). While archaeologists can safely work with some of these assumptions, special consideration must be taken into account for others and extra work must be carried out in order to counterbalance such assumptions.

### **Conclusion**

While all samples have been powdered, made into pellets, and run through the XRF spectrometer, we do not yet have conclusive results to share. As my mentor and I both are new to this process, we have decided to consult an XRF specialist to help us make sense of our results. Aaron Shugar, an inorganic chemistry conservation scientist at Buffalo State University, use-tested our created samples using a Bruker handheld TRACER III-SD XRF spectrometer. Shugar ran the prepared samples with the PXRF machine in order to compare those results with our results and to help us understand the data. Shugar, geologist Dori Farthing, and my mentor Jim Aimers have used these preliminary results to create a calibration system for PXRF in order to



contend with some of the PXRF problems mentioned above. While we do have raw data, we have not yet had the opportunity to analyze and interpret this data in relation to our goals.

In addition, as this is a new direction of study, we did not anticipate how long it would take to create and test samples and to analyze those results. Subsequently, there is a need to continue testing more samples and to assist in the analysis of the results. My mentor and I are making plans to continue working on this study and to obtain and analyze further samples. With these results we hope to understand the chemical makeup of the pottery and to determine if chemical classification corresponds with our stylistic classifications. Ultimately, through our work with classification we hope to better understand the Maya trade and exchange routes of the Postclassic period.

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